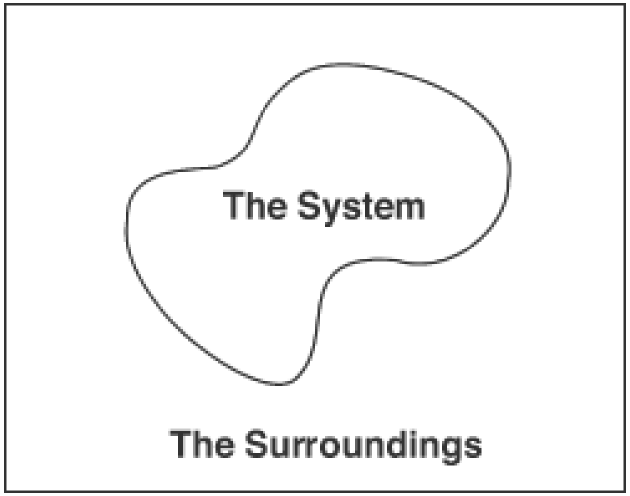
Entropy

THERMODYNAMICS

- Study of energy and inter-conversions
- 1st law of thermodynamics—law of conversation of energy
- Two parts of universe:
  - System—portion of universe that is being focused on
  - Surrounding—remaining portion of the universe

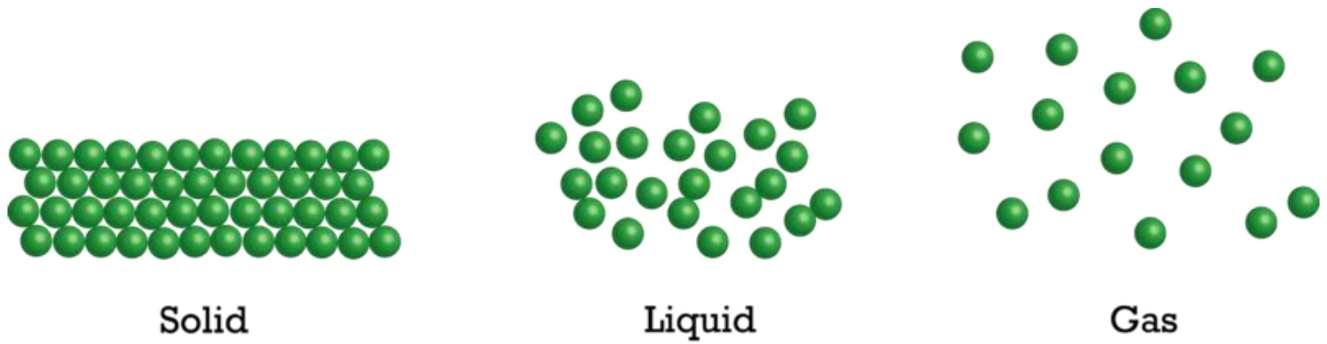


ENTROPY

- Spontaneity → a process that occurs without outside intervention
  - Driving force behind it is entropy
- Entropy
  - Symbolized by S
  - Measures the molecular randomness or disorder
  - Numerical value
    - $\Delta S > 0$, entropy is increasing
    - $\Delta S < 0$, entropy is decreasing

Positional Entropy

- Describes the number of arrangements or positions available to a system in a given state
  - Used to determine the amount of entropy a substance has in comparison with another substance
- Entropy increases from solid to liquid to gas



Example #1

- Which of the following pairs is likely to have the higher positional entropy per mole at a given temperature?
  - Solid CO_2 or $\boxed{\text{gaseous } CO_2}$
  - N_2 gas at 1.0 atm or $\boxed{N_2 \text{ at } 0.001 \text{ atm}}$

Second Law of Thermodynamics

- States that in any spontaneous process there is always an increase in the entropy of the universe
  - Entropy of the universe is always increasing
  - $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$

- Relationship of $\Delta S_{universe}$, ΔS_{system} & $\Delta S_{surroundings}$

ΔS_{system}	$\Delta S_{surrounding}$	$\Delta S_{universe}$	**Spontaneity?**
+	+	+	Yes
-	-	-	No (rxn will go in opposite direction)
+	-	?	Yes if $\Delta S_{system} > \Delta S_{surrounding}$
-	+	?	Yes if $\Delta S_{surrounding} > \Delta S_{system}$

Entropy & Enthalpy

- $\Delta S_{surrounding}$'s sign depends on heat flow
  - $\Delta S_{surrounding} = -\Delta H/T$
- $\Delta S_{surrounding}$ & enthalpy
  - Exothermic reaction = positive entropy
    - Heat flows into surroundings, increasing random motion of molecules
  - Endothermic reaction = negative entropy
    - Heat flows from surroundings, decreasing random motion of molecules

Example #2

- In the metallurgy of antimony, the pure metal is recovered via different reactions, depending on the composition of the ore. For example, iron is used to reduce antimony in sulfide ores:

$$Sb_2S_3\ (s) + 3\ Fe\ (s) \rightarrow 2\ Sb\ (s) + 3\ FeS\ (s)$$

$$\Delta H = -125\ kJ$$

Calculate $\Delta S_{surrounding}$ for each of the reaction at 25°C and 1 atm.

$$\Delta S_{surrounding} = -\frac{\Delta H}{T} = -\frac{-125\ kJ}{298\ K} = 0.419\ kJ/K$$

Entropy Changes in Chemical Reactions

- Changes in entropy for a reaction can be predicted based on the states of matter
  - For all gaseous species, the number of moles is used to determine the entropy change
    - More moles of gas in products than reactants, entropy is increasing
    - More moles of gas in reactants than products, entropy is decreasing
  - For species in all three states, creation of gases increases the entropy

Example #3

- Predict the sign of $\Delta S°$ for each of the following reactions:
  - Thermal decomposition of solid calcium carbonate:

    $$CaCO_3\ (s) \rightarrow CaO\ (s) + CO_2\ (g)$$

  - Oxidation of SO_2 in air:

    $$2\ SO_2\ (g) + O_2\ (g) \rightarrow 2\ SO_3\ (g)$$

  - Creation of gas increases the entropy
  - More moles of gas in the reactants so entropy is decreasing

Entropy Changes in Chemical Reactions

- Entropy is a state function
  - Values of different species can be determined at 25°C and 1 atm, making it standardized
  - Change in entropy from a reaction can be calculated using the following formula:

$$\Delta S^{\circ}_{reaction} = \sum S^{\circ}_{products} - \sum S^{\circ}_{reactants}$$

EXAMPLE #4

- Calculate $\Delta S°$ at 25°C for the reaction

$$2\ NiS\ (s) + 3\ O_2\ (g) \rightarrow 2\ SO_2\ (g) + 2\ NiO\ (s)$$

given the following standard entropy values:

Substance	S° (J/Kmol)
SO_2 (g)	248
NiO (s)	38
O_2 (g)	205
NiS (s)	53

$$\Delta S° = \left[2\,mol\left(248\frac{J}{Kmol}\right) + 2\,mol\left(38\frac{J}{Kmol}\right)\right] - \left[2\,mol\left(53\frac{J}{Kmol}\right) + 3\,mol\left(205\frac{J}{Kmol}\right)\right] = -149\frac{J}{K}$$